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Separation of galacto-oligosaccharides mixture by nanofiltration

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ABSTRACT

Four commercial 1812 spiral wound nanofiltration membranes were firstly applied to examine the separation performance of sugar solutions in total recycle mode of operation. Membrane NF-3 (supplied by Sepro Co. (USA)) with molecular weight cut-off of 800–1000 Da was selected for separation of a commercial galactose-oligosaccharide (GOS) mixture with low content of oligosaccharides in constant volume diafiltration (CVD) process at 50 °C and 6 bar pressure. The choosing of membrane and operation conditions for CVD process was based on a compromise between the permeate fluxes and apparent rejections of the sugar solution. In CVD course, the concentration of various sugars and the relationship between the yield and purity of oligosaccharides predicted well with mathematical models for the following situation: when the volume of every removing batch of permeate is equal to the volume of tank, the increased rate of sugar rejections is less than 8% and the decreased rate of tank concentrations is less than 15%. 90.5% monosaccharide and 52.5% lactose in the mixture were removed with NF-3 membrane in this study, and the oligosaccharides purity of 54.5% was achieved (1.5 times of the raw material), obtaining oligosaccharides yield of 70.0%.

1. Introduction

Galactose-oligosaccharides (GOS) show potential applications in functional foods and food ingredients. They can promote the growth of bifidobacteria, lipid metabolism and the adsorption of mineral in the human intestine (Gopal *et al.*, 2003; Prenosil *et al.*, 1987). Particularly, oligosaccharides, contained in human milk, are involved in the infant's defence system, the development of a specific intestinal microflora and inflammatory processes (Zopf and Roth, 1996). Usually, GOS are produced by biochemical reactions between lactose and β-galactosidases (Iwasaki *et al.*, 1996; Prenosil *et al.*, 1987). The yield of oligosaccharides (tri-, tetra- and penta-saccahrides) in the reaction is about 24–57 wt.% (Goulas *et al.*, 2002, 2007; Mozaffar *et al.*, 1984; Prenosil *et al.*, 1987). The resulting commercial GOS products contain plenty of side resultants of low molecular weight sugars such as monosaccharide (glucose, galactose) and disaccharide (lactose), degrading the performance of the GOS products. Therefore, high purity of GOS products is required not only for the scientific interest, but also their industrial application.

In industry, most of sugar separations are performed by chromatography to purify the products, and vacuum distillation to purify and condense them. The disadvantages of the process are that a large amount of time, eluant (usually water) and huge energy are needed. Nanofiltration (NF), mainly used to separate ions from solutions, has been applied for the purification, isolation or concentration of sugar solution during these years (Goulas *et al.*, 2002; Li *et al.*, 2004; Martinez-Ferez *et al.*, 2006; Vegasa *et al.*, 2006; Xu *et al.*, 2005). As compared with chromatography and vacuum distillation, less time, eluant and lower energy consumption are required by NF process. Nanofiltration membranes of GH–NF and GK–NF were used to purify and concentrate fructo-oligosaccharides in constant volume diafiltration (CVD) operation mode (Li *et al.*, 2004). Although chromatography is still the principal method for separation of maltitol mixture in industry, type D and type G membranes were proved the ability for purification and concentration of maltitol (Xu *et al.*, 2005). Martinez-Ferez *et al.* (2006) reported that a two-stage tangential ultrafiltration-nanofiltration process was possible to recovery the caprine milk oligosaccharides with tubular ceramic membranes. The Kerasep Nano and the ESP04 membranes were selected to purify xylooligosaccharide mixture containing monosaccharides obtained after rice husk autohydrolysis (Vegasa *et al.*, 2006). According to the article of Lopez Leiva and Guzman (1995), separation and concentration of oligosaccharides with NF membranes is maybe an alternative for the expensive chromatography process. This is due to the matching between nanofiltration separation (200–1000 Da) and the size of GOS mixture molecules.

Although NF-CA-50 and a series of DS-5 membranes were applied to purify model sugar solution and commercial

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Nomenclature

C_f	solute concentration in the feed solution (g/L)
C_p	solute concentration in the permeate (g/L)
CVD	constant volume diafiltration
J_p	volumetric permeate flux through the NF membrane (L/(m^2 h))
MW	molecular weight (Da)
MWCO	molecular weight cut-off (Da)
P_c	permeation factor
Pu	purity of oligosaccharides
R	apparent rejection of solute
V_c	cumulative permeate volume during CVD course (mL)
V_f	feed solution volume during CVD course (mL)
Y	yield of a solute during CVD course

Superscripts

A	micro-molecular weight sugars
B	macro-molecular weight sugars

Subscripts

f,0	original feed solution
f,f	final feed solution
p,0	original permeate solution

galacto-oligosaccharides mixture (Goulas *et al.*, 2002), they were flat sheet membranes, resulting in their only use in laboratory due to the limited effective area. On the other hand, spiral wound nanofiltration membranes are appropriate for application in separation, purification and concentration of mixture solution in industry because of the facile scale-up of their effective area. The advantage of these membranes is that their separation conditions obtained from the laboratory agree with those used in industry. High pressure of operation frequently used in industry could result in serious fouling due to the compaction of the membrane layer (Martinez-Ferez *et al.*, 2006), and the increase of operation cost. Therefore, the present study attempted to investigate the feasibility of spiral wound nanofiltration membranes at low pressure to purify GOS mixture.

Pressure, temperature and concentration dependence experiments were carried out for the selection of suitable membrane based on permeate flux and apparent rejection. Then, purification of a commercial GOS mixture was performed on the selected membrane with a CVD procedure. The concentration of different sugars and the relationship between the yield and purity of oligosaccharides were predicted with mathematical models.

2. Materials and methods

2.1. Material

Standard specimen D-glucose, α-lactose and raffinose, supplied by Sigma Chemicals (USA), were used for HPLC analysis. The ivory-white powder of GOS mixture used in the experiments was from Yantai Beer Limited Co. (China), with the specification of 18.8 wt.% monosaccharide (17.9 wt.% glucose and 0.9 wt.% galactose), 44.8 wt.% lactose and 36.4 wt.% galactose-oligosaccharides. The solution of the GOS mixture can be easily contaminated by microorganisms at appropriate temperature several hours after its preparation. Therefore, the solution was filtered using 0.45 μm micro-filtration membrane before NF experiments to avoid the fouling problems in the NF process.

2.2. Membranes and nanofiltration set-up

The four tested commercial membranes were 1812 spiral wound membrane modules. The membranes NF-2 and NF-3 were supplied by Sepro Co. (USA), assembled by Shanghai Mosu Co. (China). The manufacturer and module manufacturer of NF-1812-50 were Dow Chemical (USA) and Beijing Ande Co. (China), respectively. HBRO-1812-2 was made and assembled by Hebei R.O. Environment Tech. Co. (China). The chemical and physical characteristics of these membranes are listed in Table 1. After each experimental running with sugar solution, the membranes were washed with demineralized water for three times, and then stored in 0.5% sodium bisulfite solution at 4 °C.

The experimental apparatus (Fig. 1) was designed by Shanghai Mosu Co. (China). The feed tank (1.7 L capacity) was connected to a thermostatic water bath, which is fitted to control the system at a constant temperature. The temperature of the system was measured with temperature gauges in the pot and the exit of the loop. An electric diaphragm pump was used to pump the feed solution to the nanofiltration cell. The electric diaphragm pump has two symmetry rooms in the left and right sides, both installed two ball valves. When the electromotor drives the diaphragm to reciprocate to-and-fro, the four valves turn on and turn off alternately. At the same time, the electric diaphragm pump continuously inhales and ejects sugar solution. The pressures, controlled with a retentate valve, were indicated by two pressure gauges up and down the membrane module. The average value of the two gauges was used as applied pressure. In CVD course, the volume of dilution water and permeate was measured with measuring cylinders. To keep the feed volume constant, the flow rate of the dilution water was controlled to be equal to the permeate stream by peristaltic pump.

2.3. Experimental theory

The apparent rejection coefficient for a given solute was calculated according to Eq. (1), where C_p and C_f are the

Table 1
Membrane characteristics in this study.

	NF-2	NF-3	NF-1812-50	HBRO-1812-2
Material	Cellulose acetate	Cellulose acetate	Polyamide	Cellulose acetate
MWCO (Da)	500–600	800–1000	150–300	800–1000
Rejection NaCl (%)	60	30	50	30
Temperature range (°C)	5–50	5–50	5–50	5–30
Maximum pressure (bar)	8	8	10	10
pH range	4–7	4–7	2–11	4–7.5
Water flux (L/(m^2 h))	18–20[a]	18–20[a]	42[b]	22[a]

[a] Supplied by the manufacturers at 25 °C, 6 bar.
[b] Results obtained by the authors at 25 °C, 3 bar.

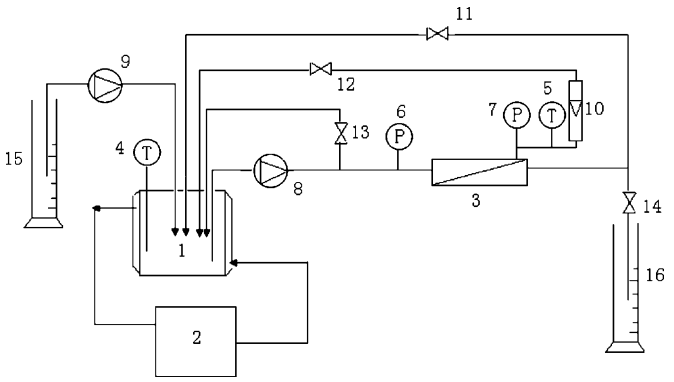

Fig. 1. Experimental apparatus: (1) feed tank, (2) thermostatic bath, (3) nanofiltration cell, (4 and 5) temperature gauge, (6 and 7) pressure gauge, (8) electric diaphragm pump, (9) peristaltic pump, (10) rotameter, (11–14) controlling valve and (15 and 16) measuring cylinder.

concentrations of the solute in the permeate and feed streams, respectively:

$$R = 1 - \frac{C_p}{C_f} \tag{1}$$

Permeation factor is:

$$P_c = 1 - R = \frac{C_p}{C_f} \tag{2}$$

CVD process is a conventional operation mode of membrane separation. As shown in Fig. 1, water from measuring cylinder is added to the feed tank at the same rate as the permeate flux in order to keep constant feed volume during the process. According to the results of Grandison and Lewis (1996), the concentration of the solute in the tank and permeate solution can be predicted by Eqs. (3) and (4) when $R \neq 0$, at the same time, the apparent rejection values remain constant throughout the process:

$$\ln\left(\frac{C_{f,0}}{C_f}\right) = (1-R)\frac{V_c}{V_f} \tag{3}$$

$$\ln\left(\frac{C_{f,0}(1-R)}{C_p}\right) = (1-R)\frac{V_c}{V_f} \tag{4}$$

where V_f and V_c are the feed volume and the cumulative permeate volume removed from the feed tank during the course. Actually, $C_{p,0} = C_{f,0}(1-R)$.

It is a multi-solute system in this study, all the solutes can be simplified to two kinds, micro-molecular solute A and macro-molecular solute B (B denotes oligosaccharides; A denotes monosaccharide and disaccharide). The purity was the percentage of the oligosaccharides in all solutes; the yield was the percentage of the original oligosaccharides remaining in the feed solution in CVD process. Purity Pu and yield Y are defined by the following equations:

$$\mathrm{Pu} = \frac{C_f^B}{C_f^A + C_f^B} \tag{5}$$

$$Y = \frac{C_{f,f}^B}{C_{f,0}^B} \tag{6}$$

where C_f^A, C_f^B are the concentrations of micro-molecular and macro-molecular solute in the feed tank, and $C_{f,f}^B$, $C_{f,0}^B$ are the concentrations of the oligosaccharides in the final and original feed solution. Based on the assumption that concentration polarization is negligible, that is, permeate factor P_c is constant, and is not dependent on the change of feed concentration, the yield can be expressed by Eq. (7) (Kilduff and Weber, 1992), and the relationship between the purity and yield can be expressed as Eq. (8) (Li et al., 2004):

$$Y = \exp\left(-P_c^B \frac{V_c}{V_f}\right) \tag{7}$$

$$\mathrm{Pu} = \left(1 + \frac{C_{f,0}^A}{C_{f,0}^B} Y^{-\Delta P_c / P_c^B}\right)^{-1} \tag{8}$$

where $\Delta P_c = P_c^B - P_c^A$.

The quantity V_c/V_f is defined as the multiple of dilution, P_c^A, P_c^B are defined as the permeation factors of micro-molecular and macro-molecular solute, and $C_{f,0}^A$, $C_{f,0}^B$ are the concentrations of micro-molecular and macro-molecular solute in the original feed solution.

2.4. Experimental procedure

All new membranes were flushed with demineralized water (conductivity is about 0.015 S/m) for 30 min to remove possible contaminants. Then, they were pre-compacted with water for 1 h at 8 bar and 25 °C to achieve a constant flux, and the initial water flux was measured for the membranes in order to compare with the data obtained after the experiment.

In the experiments of membrane selection, the total recycle mode was used to avoid change of feed concentration, in which all of permeate and retentate were recycled to the feed tank. The original feed concentration was measured after the solution was cycled for 10 min in the system. Permeate flux, J_p (L/(m^2 h)), and apparent rejection value were determined right after the system was stabilized for 30 min.

Before starting of the CVD process, the system was operated in total recycle mode for more than 30 min in order to reach the stabilized state. The original permeate flux was measured and the bank feed and permeate were sampled for the initial component analysis. Then, the permeate was removed out of the system, at the same time equivalent dilution water from the measuring cylinder was pumped into the feed tank to maintain the constant volume of feed. During the process, measuring of permeate flux and sampling of tank and permeate solution were carried out after each collecting cycle of 2 L removed permeate was finished.

The GOS mixture with more than 50% purity (about 1.5 times of the initial purity) could be directly used as functional foods or food ingredients, and could facilitate the downstream processing (ion-exchange chromatography or gel chromatography). Therefore, CVD process was stopped when the purity of oligosaccharides exceeded 1.5 times of the initial purity.

2.5. Sample analysis

Sugar solution samples were analyzed by high performance liquid chromatography (HPLC, Agilent, USA) equipped with a G1362A refractive index detector. The Aichrom-NH_2 column, 4.6 mm × 250 mm from Abel industries Co. (USA) was maintained at 30 °C, and mixture of acetonitrile and water (75:25) was used as mobile phase at a flow rate of 1 mL/min. Calibration curves were prepared with standard specimens glucose (since glucose is the major component of monosaccharides) and lactose. Trisaccharide was the major component of oligosaccharides (known from the HPLC result), therefore the calibration curve of oligosaccharides

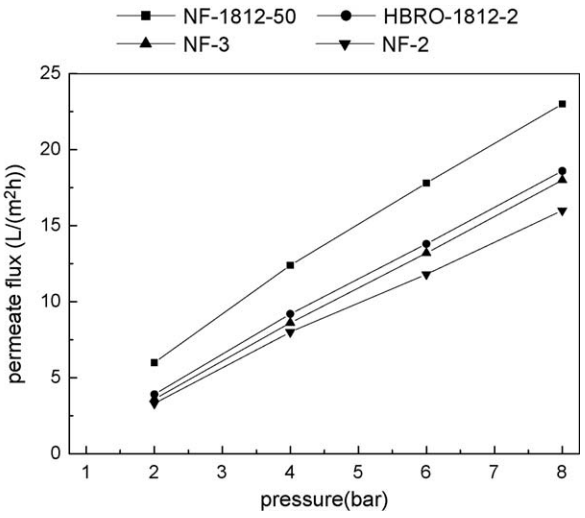

Fig. 2. Permeate flux vs. pressure for GOS mixture at 25 °C.

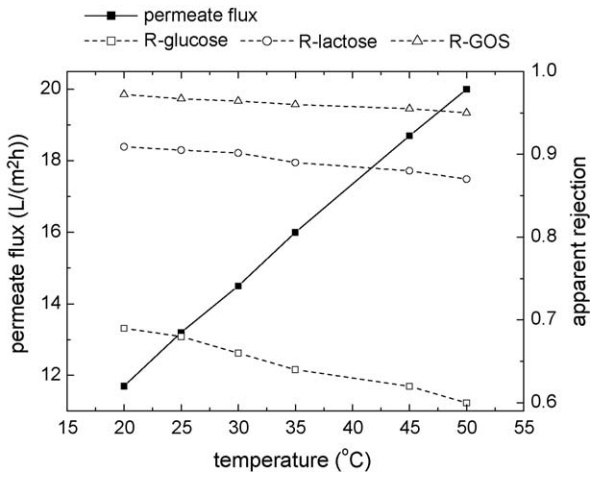

Fig. 3. Permeate flux and rejections vs. temperature for GOS mixture with NF-3 membrane at 6 bar.

was made with standard specimen raffinose. Each sample was analyzed twice and their average value was used.

3. Results and discussion

3.1. Selection of nanofiltration membrane and operation condition

3.1.1. Effect of pressure

With both retentate and permeate recycled to the feed bank, pressure dependence experiments were carried in order to select the suitable membrane according to permeate flux and solute apparent rejection. After the system was stabilized for half an hour, the permeate flux of GOS mixture (20 g/L) were measured from 2 to 8 bar at 25 °C (Fig. 2). The apparent rejection values of the membranes for various sugars were shown in Table 2.

The membranes with high permeate flux of solution, low rejection of micro-molecular solute and high rejection of macro-molecular solute were expected. As shown in Fig. 2 and Table 2, NF-2 presents the lowest permeate flux and the highest rejection of monosaccharides. NF-1812-50 exhibits the largest permeate flux, but the highest rejection of lactose and oligosaccharides, which was suitable to concentration but not separation of GOS mixture.

Table 2
Comparison of apparent rejection values of the membranes for various sugars at 25 °C.

	2 bar	4 bar	6 bar	8 bar
NF-2				
Glucose	0.64	0.72	0.83	0.89
Lactose	0.89	0.91	0.93	0.94
Oligosaccharides	0.96	0.97	0.98	0.98
NF-3				
Glucose	0.51	0.64	0.68	0.72
Lactose	0.82	0.85	0.88	0.91
Oligosaccharides	0.93	0.95	0.96	0.97
HBRO-1812-2				
Glucose	0.52	0.67	0.74	0.79
Lactose	0.83	0.86	0.89	0.91
Oligosaccharides	0.94	0.96	0.97	0.97
NF-1812-50				
Glucose	0.64	0.71	0.75	0.78
Lactose	0.96	0.98	0.98	0.99
Oligosaccharides	0.99	0.99	0.99	0.99

NF-3 and HBRO-1812-2 are appropriate membranes due to their permeate flux and relative large difference in rejections between macro-molecular and micro-molecular sugars. The optimum pressure for a separation process should also be a compromise between the permeate flux and apparent rejection.

3.1.2. Effect of temperature

The effect of temperature on the permeate flux and apparent rejections of the sugars was studied with NF-3 membrane at 6 bar. With the temperature increased from 20 to 50 °C (the operation temperature of NF-3 is 5–50 °C), the permeate fluxes increased linearly and the apparent rejections of the sugars decreased (Fig. 3). This is due to the reduced viscosity of the feed solution and the increased effective pore diameter of the membranes with increasing temperature, which agrees with the results of other investigators (Aydogan *et al.*, 1998; Goulas *et al.*, 2002; Xu *et al.*, 2005). Therefore, it is concluded that high temperature is favorable for the separation of the GOS mixture.

3.1.3. Effect of concentration

The effect of feed concentration on the separation of the GOS mixture with HBRO-1812-2 and NF-3 membranes was studied under pressure of 6 bar and the highest permitted temperature in total recycle mode of operation. A low concentration of feed solution was prepared in demineralized water and placed into the feed tank. After each measurement, appropriate powder material was added into the initial solution to obtain a series of higher concentration. The effect of feed concentration on the permeate flux was shown in Fig. 4, the apparent rejection values of various sugars at varying feed concentration of NF-3 membrane were shown in Fig. 5.

As shown in Fig. 4, the permeate flux decreased with the increase of feed concentration due to the decrease in the pressure driving force and the accretion of concentration polarization. The reason of the decrease in the pressure driving force is the increase of osmotic pressure with the increase of feed concentration as the applied pressure keeps constant (driving force = applied pressure − osmotic pressure). The permeate flux of NF-3 is higher than that of HBRO-1812-2 mainly because of different operation temperature at 50 and 35 °C. On the other hand, the feed solution became somewhat turbid when the experiment was carried for a certain time at 35 °C with HBRO-1812-2 membrane. This may be caused by various microorganisms under normal appropriate temperature.

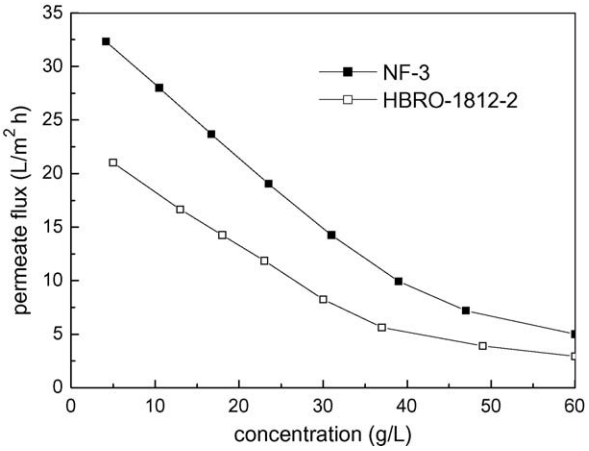

Fig. 4. Permeate flux vs. concentration for GOS mixture with NF-3 and HBRO-1812-2 membranes at 6 bar, 50 and 35 °C, respectively.

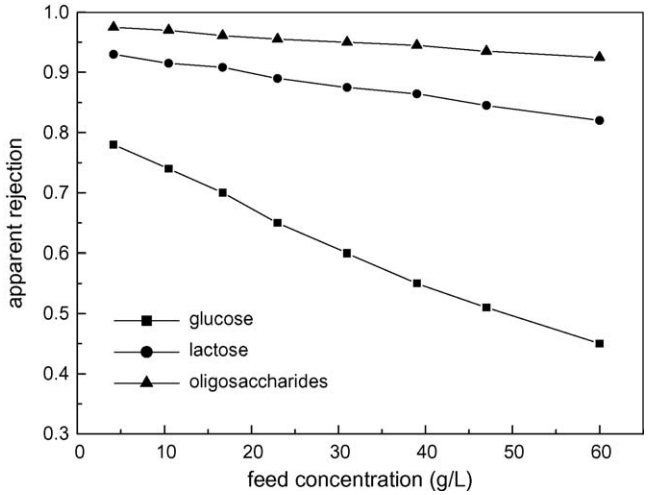

Fig. 5. Rejection values of sugars vs. feed concentration for GOS mixture with NF-3 at 6 bar and 50 °C.

Therefore, temperature control is important in the GOS CVD process in industry. If the process is carried around 35 °C, sterilization of the feed solution is required.

The apparent rejections of sugars decreased with the increase of feed concentration (Fig. 5). However, the rejection of neutral species at constant pressure is independent on concentration (Bowen and Welfoot, 2002). Therefore, the mainly reason for the decrease of the sugar rejections is also due to the decrease in the pressure driving force, induced by the increase of osmotic pressure as the applied pressure keeps constant. The rejection of oligosaccharides decreased a little, however, the rejection of glucose and lactose decreased a lot with the increase of feed concentration, resulting in the increasing rejection difference between oligosaccharides and micro-molecular sugars, which was favorable for the separation of the GOS mixture. Therefore, the optimum feed concentration must be a compromise between the permeate flux and rejection of the sugar solution.

Based on the above-mentioned analysis, the optimum NF membrane for the separation of the GOS mixture is NF-3, and the optimum operation conditions are 50 °C, 6 bar pressure and feed concentration about 50 g/L.

3.2. Constant volume diafiltration

NF-3 membrane was selected to separate the GOS mixture for the CVD process. The CVD process was carried out at 50 °C, 6 bar pressure and 50.5 g/L initial concentration of the GOS mixture (which is analyzed with HPLC after the feed solution cycled for 10 min). During the separation, measuring of permeate flux and sampling of feed tank and permeate were carried out after each collecting cycle of 2 L removed permeate was finished. Trace fouling appeared in the experiments, which is concluded from the almost same permeate fluxes of demineralized water before and after the NF process.

As shown in Fig. 6, during the process of CVD, the permeate flux increased continually owing to the decrease of concentration polarization resulting from lower concentration and decreased viscosity of feed sample. The concentration of various sugars in the permeate and tank solution were shown in Fig. 7(a) and (b). All the concentration predicted with the Eqs. (3) and (4) also was presented in these figures. The average apparent rejection values were used in Eqs. (3) and (4). If R is allowed to vary with time, the predicted concentration will fit to the actual concentration. Grandison and Lewis proved that Eqs. (3) and (4) were applicable when the rejection rate of the solute remained constant throughout the CVD process, which required the total sugar concentration to remain nearly constant in the whole CVD process (Grandison and Lewis, 1996). In this study, although the rejection of glucose increased from 0.52 to 0.73 (Fig. 7(c)) and the whole sugar concentration decreased from 50.5 to 24.0 g/L (Fig. 6), the concentrations of various sugars can be still predicted. Therefore, it is considered that Eqs. (3) and (4) can be used in more wide operation range. When the volume of every removing batch of permeate is equal to the volume of tank, the increased rate of sugar rejections was less than 8% and the decreased rate of tank concentrations was less than 15%. In this case, the model equations can predict the CVD process in this study.

Fig. 7(c) shows the relationship between the yield of various sugars and cumulative permeate volume during CVD process at 50 °C, 6 bar. The yield of glucose decreased rapidly with increasing of cumulative permeate volume, and only 9.5% glucose remained in the feed tank when cumulative permeate volume reached 10 L, which was 5.9 times of the feed solution. The yield of lactose and oligosaccharides also decreased, however, which is much lower than that of glucose. This is caused by lower glucose rejection and relative higher lactose and oligosaccharides rejections during CVD process (Fig. 7(c)). It is concluded from Fig. 7(c) that the difference in rejections between oligosaccharides (MW more than 504) and lactose (MW 342) is less than that between glucose (MW 180) and lactose, moreover, the rejections of oligosaccharides and lactose

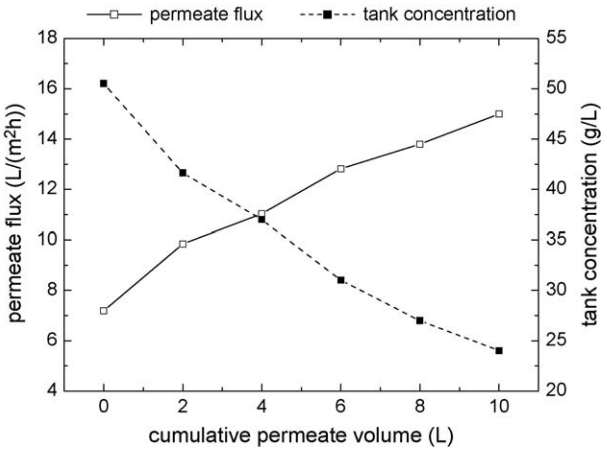

Fig. 6. Permeate flux and tank concentration vs. cumulative permeate volume at 50 °C and 6 bar in CVD course.

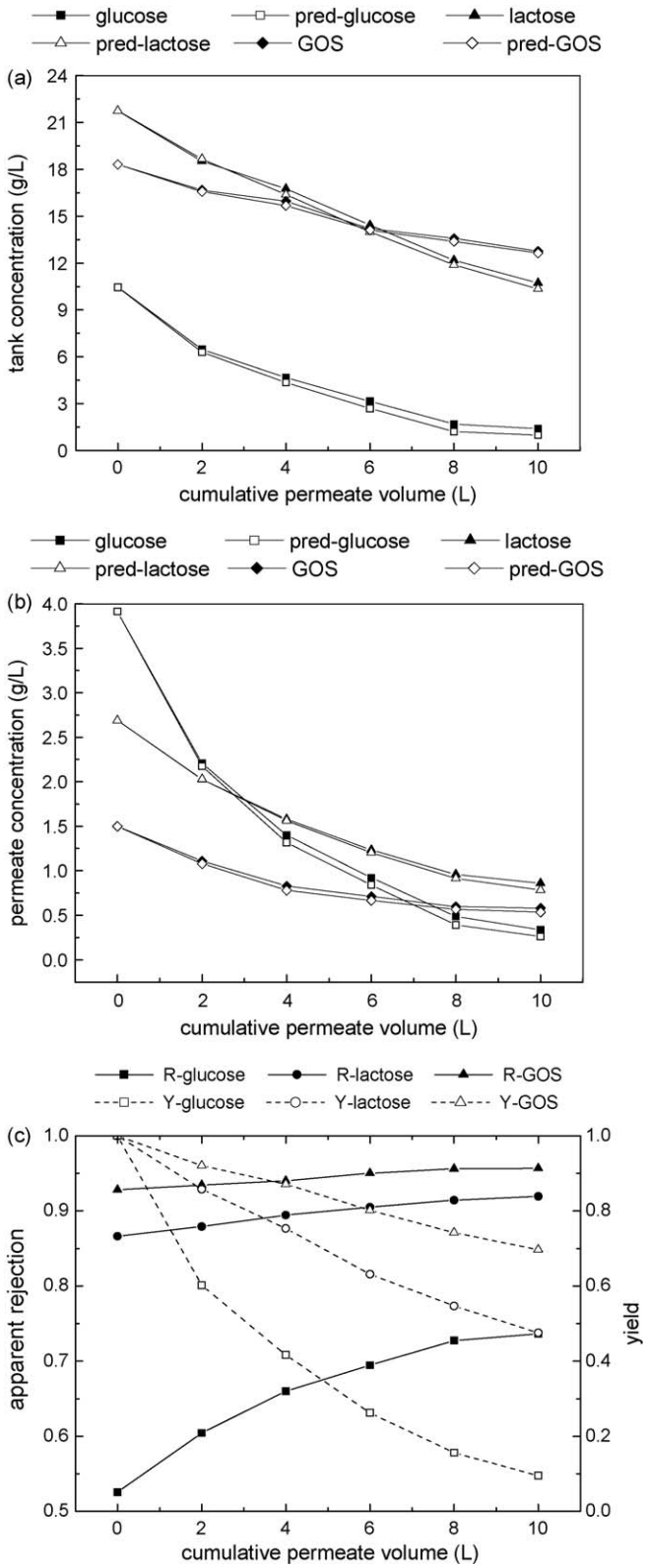

Fig. 7. CVD process with NF-3 membrane at 50 °C and 6 bar. (a) Experimental and predicted feed concentration vs. cumulative permeate volume. (b) Experimental and predicted permeate concentration vs. cumulative permeate volume. (c) Rejection and yield vs. cumulative permeate volume.

changed slightly with the decrease of the tank concentration in CVD process, whereas the rejection of glucose increased obviously. This indicates that the rejections are not only dependent on the solute molecules but also on other factors such as the different spatial configuration of monosaccharide, disaccharide and oligosaccharides.

3.3. Purity and yield of oligosaccharides

Eqs. (7) and (8) show that low permeation factor of macromolecular solute and large permeation factor difference between micro-molecular and macro-molecular solute caused high purity and yield of the oligosaccharides. There are three types of commercial NF membranes at present. The first type of NF membranes such as NF-1812-50 and NF-2 membranes present high rejections of oligosaccharides and disaccharide, and low rejection of monosaccharide. They can separate monosaccharide from oligosaccharides, however, most of disaccharide remained in the feed solution at the same time. The second type of NF membranes with appropriate pore size has high rejection of oligosaccharides and low rejection of disaccharide and monosaccharides. These membranes can separate monosaccharide and oligosaccharides with part of disaccharide remained in the feed solution. NF-3 is such type of membrane, which gave yield 70 and 9.5% for the oligosaccharides and monosaccharides at 6 bar, and 47.5% of the disaccharide were also found in the feed. In addition, similar membranes ESP04 and Kerasep Nano were used to purify xylooligosaccharides mixture. 70–78% of the oligosaccharides was obtained in feed, while 77–83% of monosaccharides were found in the permeate (Vegasa *et al.*, 2006). The third type of NF membranes has lower disaccharide rejections as compared to the above-mentioned membranes, and relative larger difference in rejections between disaccharide and oligosaccharides, but also presented relative lower rejections of oligosaccharides, thus resulting in a great loss of oligosaccharides in CVD course. DS-GE and UF-CA-1 were such type of membranes, having the rejections of oligosaccharides and disaccharide about 70–71% and 41–45% (Goulas *et al.*, 2002). GH–NF and GK–NF membranes, presenting the rejections of 1-kestose (GF_2) 76 and 64%, the rejections of disaccharide 45 and 35%, were used to purify fructo-oligosaccharides (Xu *et al.*, 2005). Such type of membranes may be preferable choice to separate disaccharide from oligosaccharides, whereas the permeates should be recovered for further purification in order to reduce the loss of oligosaccharides, which results in more energy cost and operation complexity.

Actually, as shown in Eq. (8), not only the permeation factors of solutes but also the initial composition of mirco-molecular and macro-molecular solute is important factor affecting the relationship between purity and yield of oligosaccharides product. Because the difference of rejections between oligosaccharides and lactose is less than the difference of rejections between oligosaccharides and

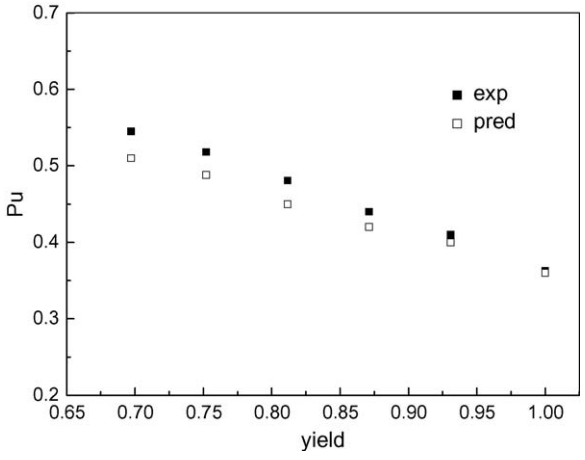

Fig. 8. Relationships between purity and predicted purity with yield.

glucose, the content of micro-molecular lactose is much more important. If the initial GOS mixture has high concentration of oligosaccharides and low concentration of lactose, NF process can obtain satisfactory oligosaccharides yield and purity. However, many GOS mixture products contain 24–40 wt.% of oligosaccharides, more than 40 wt.% of lactose and small amount of monosaccharide (Goulas *et al.*, 2007; Mozaffar *et al.*, 1984; Prenosil *et al.*, 1987). In this study, with the specifications of 18.8 wt.% monosaccharide, 44.8 wt.% lactose and 36.4 wt.% oligosaccharides, 90.5% monosaccharide and 52.5% lactose in the mixture were removed with NF-3 membrane, and the oligosaccharides purity of 54.5% was achieved (1.5 times of the raw material), obtaining oligosaccharides yield of 70.0%.

Fig. 8 shows the relationship between experimental purity and predicted purity with yield of oligosaccharides, the experimental purity of oligosaccharides was calculated with Eq. (5), and predicted purity was calculated with Eq. (8). The results indicated that Eq. (8) predicted the purity values well, the deviation between the experimental and predicted purity was little than 6%. Namely, although Eq. (8) was obtained based on the assumption that concentration polarization is negligible, that is, permeate factor P_c is constant, it could be used to predict the relationship between purity and yield well as long as the solute permeate factor and tank concentration changed proportionally and slowly. In fact, from Fig. 8, it can be seen that, the yield and purity of oligosaccharides basically showed a linear relationship with the trendline $Pu = -0.6294\,Y + 0.987$, $R^2 = 0.9883$.

4. Conclusions

Four commercial 1812 spiral wound NF membranes were firstly applied for the separation of GOS mixture in order to agree with the separation conditions in industry. Therefore, the study provided some significant data and information for the industrialization in the separation of oligosaccharides mixture by nanofiltration. High pressure can induce serious fouling due to the compaction of the membrane layer, which inevitably results in high energy cost. Hence, operation pressure of lower than 8 bar pressure was adapted to test the separation performance of the membranes with sugar solutions.

Effects of operation pressure, temperature and feed concentration on permeate flux and apparent rejections of sugars were characterized in full recycle mode of operation to select of optimum NF membrane and operation condition. The permeate fluxes and apparent rejection of sugars increased with increasing pressure for a given membrane. With increase of temperature, the permeate fluxes increased and rejections decreased when other parameters were fixed. On the other hand, both of the permeate fluxes and rejections of sugars decreased with increasing feed concentration. The selection of optimum NF membrane and operation conditions for a separation process was a compromise between the permeate fluxes and rejections of sugar. Therefore, NF-3 was chosen to perform CVD purification at 50 °C and 6 bar with a commercial GOS mixture.

In CVD course, the concentrations of various sugars and the relationship between purity and yield were predicted with models for the following situation: when the volume of every removing batch of permeate is equal to the volume of tank, the increased rate of sugar rejections is less than 8% and the decreased rate of tank concentrations is less than 15%.

Not only the permeation factors ($P_c^B, \Delta P_c$) of solutes but also the initial composition of the mixture, especially the content of disaccharide, have a significant influence on the relationship between purity and yield of oligosaccharides product, because the difference in rejections between oligosaccharides and lactose was less than the difference in rejections between oligosaccharides and glucose. In this study, with the low purity of raw material (18.8 wt.% monosaccharide, 44.8 wt.% lactose and only 36.4 wt.% galactose-oligosaccharides), 90.5% monosaccharide and 52.5% lactose were removed from the mixture, 54.5% of the oligosaccharides purity was obtained (1.5 times of the raw material) and oligosaccharides yield reached 70.0% using NF-3 membrane.

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